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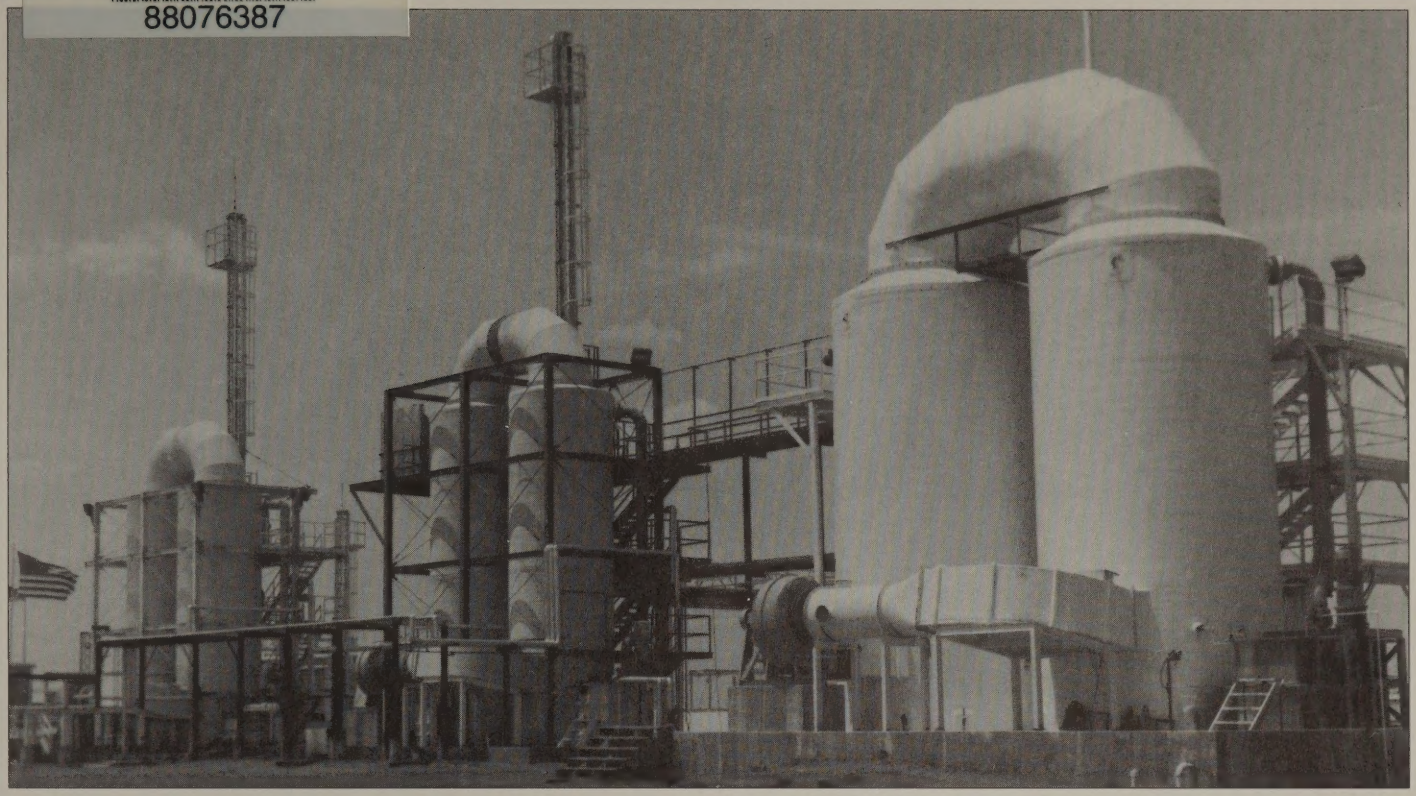

IODINE

By Phyllis A. Lyday

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IODINE

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MINES

T S Ary
Director

October 1991

Contents

Tables

COVER PHOTO:
Iodine plants in Vici, OK. (Photo is courtesy of IoChem Corp.)

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IODINE

By Phyllis A. Lyday

Mrs. Lyday, a physical scientist with the U.S. Bureau of Mines, has been the commodity specialist for iodine for 12 years. Domestic survey data were prepared by Blanche Hughes, mineral data assistant; and international data tables were prepared by William L. Zajac, Chief, Section of International Minerals.

Three producers of crude iodine supplied approximately one-half of domestic demand; the remainder was imported. Because some exports and imports are in product categories rather than crude products, net imports are not clearly developed. The major world producer, Japan, produced iodine from brines associated with gas production. The second largest producer, Chile, produced iodine as a coproduct of sodium nitrate.

DOMESTIC DATA COVERAGE

Domestic production data for iodine are developed by the U.S. Bureau of Mines from a voluntary survey of U.S. operations. Of the four operations to which a survey request was sent, four responded, representing an estimated 100% of the total production shown in table 6.

BACKGROUND

Definitions, Grades, and Specifications

Commercial crude iodine normally has a minimum purity of 99.5%. Resublimed iodine is usually 99.9% pure. Most iodine is converted for industrial use to potassium iodide, sodium iodide, and other inorganic compounds, as well as numerous organic compounds.

Geology-Resources

Iodine occurs in rocks and soils, surface and underground brines, and in caliche ores. Michigan brines contain about 30 parts per million (ppm) of iodine in the Sylvania Formation of Devonian age. California brines contain 30 to 70 ppm of iodine in brines associated with oilfields in the middle Miocene age, Monterey Formation, and the lower Pliocene age Repetto Formation. Louisiana brines contain about 35 ppm of iodine. In Oklahoma, iodine concentrations associated with oil and gas range between 150 to 1,200 ppm. In Woodward County, OK, the iodine occurs in the Morrowan Formation of Pennsylvania age.

Extensive iodine-bearing nitrate ores occur in caliche deposits in a belt several hundred kilometers long in the Atacama Desert of northern Chile. The ore layers are 1 to 3 meters thick, usually flat or gently dipping and near the surface. Evaporate minerals such as lautarite (CaI_2O_6) and dietzeite ($2CaO \cdot I_2O_5 \cdot CrO_3$) occur as cementing material in unconsolidated surface material or as veins and impregnations in bedrock.

Japanese brines contain 50 to 135 ppm of iodine in the Kiwada, Otadai, and Umegase Formations of the Kazusa Group of Pliocene age. The major iodine-producing area was the southern Kanto Gasfield, which extends over Chiba, Tokyo, and Kanagawa Prefectures. Iodine was produced in the Niigata and Nakojo Gasfields in Niigata Prefecture, on the Sea of Japan side of central Japan, and the Sadowara Gasfield in Miyazaki Prefecture, southern Kyushu.

In Indonesia, iodine occurs with trace amounts of bromine in brines associated with oil. The most important iodine-producing area is the Gujangon anticline of sandstone and diatomaceous marls of the Upper Pliocene, Kailiberg Formation.

On Okinawa, iodine occurs in concentrations of about 85 ppm in the Tomigusuku Formation of the Shimajiri Group of late Miocene-early Pleistocene age.

Technology

Processing.—In the Japan and United States, iodine is removed from brines by processes that separate the brines from any associated hydrocarbons. In the blowing-out process, brine is acidified and iodine is liberated by reducing the pH to about 3. A countercurrent stream of air transports the liberated iodine to a second tower in which the iodine is absorbed by a solution of hydriodic acid. The iodine settles, is filtered, and melted under concentrated acid. Brine stripped of iodine is treated and then reinjected into its subsurface formation of origin.

In the absorption process, brine is passed through an absorber and the waste brine is neutralized and sent to a disposal well. The absorbent laden with iodine is treated with an alkaline solution to regenerate the absorbent and eluted iodine as sodium iodide. Iodide is precipitated under acid.

Japanese plants also use an ion-exchange resin. Upon saturation, the iodine is eluted using a caustic solution that regenerates the resin. Iodine is then processed with a sodium chloride solution and melted under acid.

Chilean caliche deposits are mined by open pit methods. The ore is leached with an alkaline solution to dissolve the iodine as sodium iodate, which is converted to sodium iodide. Iodine is precipitated by reacting with additional alkaline solution. The precipitated iodine is filtered in bag filters and the iodine free-leach solution is returned to the nitrate-leaching cycle.

Recycling.—The removal of ionic silver from photographic processing solutions, such as developer, fixer, bleach fixers, and washwaters, can be accomplished with halogens such as iodine and an adsorbent. Photographic silver is commonly recovered by electrolytic methods if the concentration is greater than 500 ppm. Absorbents such as natural and synthetic zeolites, activated alumina, activated silica, fuller's earth, and ion-exchange

resins are used to recover low concentrations of silver from a stream.[1]

Economic Factors

Prices.—In the past, changes in the official price of crude iodine have been initiated during shortages. Because iodine cannot be substituted in radiopaque, animal feeds, catalysts, and stabilizers readily, shortages tend to cause the accumulation of inventories to ensure an adequate supply. An adequate supply tends to lower and stabilize the price.

Costs.—Electrical costs for maintaining the pumps to bring the brine to the surface, for air-blowing the iodine, and for reinjecting the brine are major components of maintenance costs. Capital costs have been estimated at $20 per pound of annual iodine production. These costs include high-quality stainless steels because iodine is highly corrosive. In addition, the brine must be leased from private landowners over large acreage for many years. The principal material cost is for chlorine because 1 pound is required for every 1.4 to 1.8 pounds of iodine produced.

Tariffs.—Crude and resublimed iodine enter the United States duty free. Calcium and cuprous iodine has a 25% ad valorem for non-most-favored-nation status. Potassium iodide has a 2.8% ad valorem for most-favored-nation status and 7.5% ad valorem for non-most-favored-nation status.

Depletion Provisions.—The domestic and foreign depletion allowances for mined iodine are 14% of gross income, and they may not exceed 50% of net income without the depletion deduction. The domestic and foreign depletion allowances for minerals from brine wells are 5%.

Operating Factors

Environmental Requirements.—The reinjection of waste brine is a limiting factor to the production of iodine. During 1982, the Environmental Protection Agency (EPA) reclassified disposal wells for spent brine after halogen extraction as class 5 wells. All of the reinjection wells for iodine in Oklahoma were drilled for the reinjection of waste associated with brine production or oil and gas effluent.

Toxicity.—Iodine is absorbed by the body and concentrated in the thyroid. Iodine is essential to higher animals and humans. A normal person requires about 75 milligrams of iodine per year, which is usually consumed as iodized salt that contains one part sodium or potassium iodide to 100,000 parts of sodium chloride. Iodine deficiency is a major cause of goiter.

The maximum safe concentration for short-term air environment exposure of up to 1 hour is 1.0 ppm. Exposure of the lungs and eyes can be irritating at concentrations of 0.1 ppm and should be avoided. Greater exposure can cause severe irritations to the eyes and the respiratory tract and may lead to pulmonary edema.

In 1979 and 1986, nuclear accidents caused the release of radioactive iodine I^{131} into the atmosphere. A dosage of potassium iodide (KI) administered prior or shortly after exposure of radioactive iodine can block the intake of radiation to the thyroid. The dosage must be repeated if exposure continues. Replenishing the thyroid with KI prevents the thyroid from using radioactive I^{131} for normal metabolic needs.

TABLE 1

TIME-PRICE RELATIONSHIPS FOR CRUDE IODINE

Year	Average annual c.i.f. value, dollars per pound		Average annual c.i.f. value, dollars per kilogram	
	Actual price	Based on constant 1990 dollars	Actual price	Based on constant 1990 dollars
1970	$1.15	$3.60	$5.59	$17.50
1971	1.58	4.68	3.48	10.32
1972	1.64	4.64	3.62	10.22
1973	1.72	4.57	3.79	10.07
1974	1.86	4.53	4.10	9.99
1975	2.21	4.90	4.87	10.80
1976	2.13	4.44	4.70	9.79
1977	1.05	2.05	2.31	4.52
1978	2.21	4.03	4.87	8.87
1979	3.37	5.64	7.43	12.43
1980	4.72	7.24	10.41	15.97
1981	6.03	8.44	13.29	18.60
1982	5.97	7.85	13.16	17.31
1983	5.57	7.05	12.28	15.54
1984	4.90	5.98	10.80	13.19
1985	5.38	6.38	11.86	14.06
1986	5.68	6.56	12.52	14.47
1987	6.92	7.75	15.26	17.09
1988	7.92	8.59	17.46	18.93
1989	7.70	8.02	16.98	17.67
1990	6.26	6.26	13.80	13.80

Source: Bureau of the Census.

ANNUAL REVIEW

Legislation and Government Programs

The June 21 Federal Register announced an ad hoc meeting of experts in the field of nuclear medicine and potassium iodide issues to solicit relevant scientific and medical information. The meeting was sponsored by the Center for Environmental Health and Injury Control of the Centers for Disease Control, U.S. Department of Health and Human Services.

The State of Oklahoma passed a bill to empower the Oklahoma Corp. Commission (OCC) to regulate individuals or companies that produce iodine from underground saltwater. Oklahoma is the only state where iodine is produced. The bill is expected to simplify the producers' obligations by requiring OCC approval for all iodine production. The courts have held that brine in the ground belongs to the surface owner, while associated natural gas belongs to the mineral owner. The bill puts natural gas produced with iodine-bearing brine water in a high-priority production classification.

Strategic Considerations

The National Defense Stockpile contained 6.1 million pounds of crude iodine. The stockpile goal remained at 2.6 million kilograms (kg) (5.8 million pounds). The Defense Logistics Agency of the U.S. Department of Defense disposed of 5,000 kg of excess material during fiscal year 1990.

Production

IoChem Corp., 2 miles east of Vici, Dewey County, OK, produced iodine by the blowing-out process. The majority of production was shipped to Schering AG, Federal Republic of Germany, under a long-term contract. IoChem was reported to have nine production wells and four injection wells with a total production capacity of 1,200 kilograms. North American Brine Resources operated miniplants at Dover in Kingfisher County, OK. The plant is at an oilfield reinjection disposal site. Iodine concentrations ranged up to 1,200 ppm. The company also operated a plant at the border of Woodward and Harper Counties. Woodward Iodine Corp., a subsidiary of Asahi Glass Co. of Japan, operated a plant in Woodward County that produced iodine from brines using the blowing-out process.

Consumption and Uses

Iodine was used primarily in animal feed supplements, catalysts, inks and colorants, pharmaceutics, photographic equipment, sanitary and industrial disinfectants, stabilizers, and radiopaque medium. Other smaller uses included production of batteries, high-purity metals, motor fuels, iodized salt, and lubricants.

The lithium-iodine battery was the first commercially successful lithium battery and is unusual because of its in situ growth of electrolytes. Superior charge transfer is achieved using an iodine compound with powdered iodine. Layers of lithium iodide act as both electrolyte and separator and are self-sealing in the event of a crack. Thus, the batteries are intrinsically reliable and withstand abuse.[2]

TABLE 2

U.S. CONSUMPTION OF CRUDE IODINE, BY PRODUCT

Product	1989		1990	
	Number of plants	Consumption (thousand kilograms)	Number of plants	Consumption (thousand kilograms)
Reported consumption:				
Resublimed iodine	7	143	7	143
Hydriodic acid	3	49	2	W
Calcium iodate	(1)	(1)	(1)	(1)
Calcium iodide	3	119	3	110
Cuprous iodide	3	15	3	17
Potassium iodide	6	829	5	627
Potassium iodate	5	56	4	62
Sodium iodide	4	46	4	81
Other inorganic compounds	14	821	15	1,133
Ethylenediamine dihydroiodide	4	398	4	433
Other organic compounds	8	426	8	448
Total	2 31	2,902	2 30	3,054
Apparent consumption	XX	4.8	XX	5.3

W Withheld to avoid disclosing individual company proprietary data; included with "Other inorganic compounds." XX Not applicable.
[1]Included with calcium iodide.
[2]Nonadditive total because some plants produce more than one product.

Prices

The average declared c.i.f. value for imported crude iodine was $15.19 per kg ($6.90 per pound). The average declared c.i.f. value for imported crude iodine from Japan averaged $14.90 per kg ($6.76 per pound). The average declared c.i.f. value for iodine imported from Chile was $15.51 per kg ($7.04 per pound).

Quoted yearend U.S. prices for iodine and its primary compounds are shown in table 3.

Foreign Trade

The U.S. Government adopted the Harmonized Commodity Description and Coding System (Harmonized System) as the basis for its export and import tariff and statistical classification systems. The system is intended for multinational use as a basis for classifying commodities in international trade for tariff, statistical, and transportation purposes. The Harmonized System as proposed includes resublimed and crude iodine under the same code, and the duty rate is free. During 1989 and 1990, exports to Santa Domingo were incorrectly placed into the iodine category. A test of correct reporting is to calculate price per kilogram and compare this value with the prices shown above. Values that differ significaly could be a result of being placed in the wrong category.

World Review

Capacity.—The data in table 4 are rated capacity for plants as of December 31, 1990. Mine capacity for iodine is based on rated capacity as reported by the company, another government agency, or another published source.

Chile.—Sociedad Química y Minera de Chile (SOQUIMICH) was the largest producer of iodine in Chile. The María Elena and Pedro de Valdivia plants

TABLE 3

YEAREND 1990 PUBLISHED PRICES OF ELEMENTAL IODINE AND SELECTED COMPOUNDS

	Dollars per kilogram[1]	Dollars per pound[1]
Calcium iodate, FCC drums, f.o.b. works	$16.42	$7.45
Calcium iodide, 50-kilogram drums, f.o.b. works	$23.65– 25.65	$11.62–12.07
Eythlenediamine dihydriodide	16.64– 20.39	7.55– 9.25
Hydrodic acid, f.o.b. works	18.19– 19.95	8.25– 9.05
Iodine, crude, drums	13.00– 14.00	5.89– 6.34
Potassium iodide, U.S.P., drums, 5,000-pound lots, delivered	26.48	12.01
Iodine, U.S.P.	17.00	7.70
Sodium iodide, U.S.P., crystals, 5,000-pound lots, drums, freight equalized	36.38	16.50

[1]Conditions of final preparation, transportation, quantities, and qualities not stated are subject to negotiations and/or somewhat different price quotations.

Source: Chemical Marketing Reporter. V. 238, No. 27, Dec. 31, 1990, pp. 36–38.

TABLE 4

U.S. IMPORTS FOR CONSUMPTION OF CRUDE IODINE, BY TYPE AND COUNTRY

(Thousand kilograms and thousand dollars)

Country	1989		1990	
	Quantity	Value[1]	Quantity	Value[1]
Iodine, crude:				
Belgium	30	545	—	—
Canada	(2)	9	—	—
Chile	1,014	18,298	1,321	18,598
Germany, Federal Republic of	(2)	1	—	—
Japan	2,251	39,751	(2)	53
Mexico	13	178	1,798	24,295
Sweden	(2)	13	20	307
United Kingdom	—	—	(2)	2
Total[3]	3,309	58,795	3,139	43,256
Iodide, potassium:				
Germany, Federal Republic of	1	28	(2)	4
India	7	121	17	215
Italy	9	31	9	23
Japan	—	—	1	18
United Kingdom	(2)	5	2	37
Total	17	185	29	297
Grand total[3]	3,326	58,980	3,168	43,553

[1]Declared c.i.f. valuation.
[2]Less than 1/2 unit.
[3]Data may not add to totals shown because of independent rounding.

Source: Bureau of the Census.

TABLE 5

WORLD IODINE ANNUAL PRODUCTION CAPACITY,[1] DECEMBER 31, 1990, RATED CAPACITY[2]

(Thousand kilograms)

Country	Capacity
North America: United States	1,200
South America: Chile	3,800
Europe: U.S.S.R.	2,000
Asia:	
China	500
Indonesia	4
Japan	7,000
Total	7,600
World total	[3]15,000

[1]Actual capacity limited by brine supply.
[2]Includes capacity at operating plants as well as at plants on stand-by basis.
[3]Data do not add to total shown because of independent rounding.

produced iodine, sodium nitrate, potassium nitrate, and sodium sulfate. SOQUIMICH continued to operate a plant at Puelma. Installed capacity was reported at 6,000 tons per year.

SOQUIMICH had a joint venture with Israel Chemicals Ltd. named Compania Quimica Internacional de Desarrollo (IDC Co.). In March, Israeli Chemicals of Israel purchased 10.5% of SOQUIMICH's shares valued at $30 million from the Bankers Trust New York Corp. of the United States.[3]

Other companies active in iodine production were Amsterdam Chemical Pharmaceutical Minera (ACF Minera), a joint venture of the Sociedad Contractual Minera Lagunas and the Amsterdam Pharmaceutical Co. of the Netherlands. ACF Minera operated a plant using nitrate tailings as the iodine source.

Also actively producing iodine from nitrate tailings was Compania de Salitre y Yodo de Chile (Cosayach), a subsidiary of Cia. Minera del Norte. Cosayach inaugurated a plant in November. A feasibility study completed by Davy McKee Worldwide Corp. established that the Yolanda nitrate and iodine project near Taltal was both financially viable and technically feasible. The study suggests an annual output of 1,360 metric tons of iodine and 250,000 metric tons of potassium nitrate. Recoverable resources are

reported at 40,500 tons of iodine. North Lily Mining is operator of the company and will receive a 10% net profit interest. Kap Resources, the owner of the property, merged with its joint-venture partner Atacama Resources.[4] A second location was being studied at Yumbes Pampa south of the Yolanda site.

In May, Chile Hunt Oil Co. reported the discovery of gas in the Salar de Atacama at a depth of 4,500 meters. The availability of gas for the generation of low-cost electric power could increase the economic viability of other projects in the region.[5]

Indonesia.—The only producer of crude iodine was the state-owned pharmaceutical firm, P. T. Kimia Farma, that operated a plant at Watudakon near Mojokerto, East Java.

Japan.—Production of iodine was from underground brines associated with natural gas. Japan was the world's leading producer of iodine in 1989. Six companies operated 17 plants with a total production capacity of 9 million kilograms per year.

OUTLOOK

Iodine production capacity in the United States and Chile has doubled during the past decade, ensuring an adequate world supply. Uses for iodine in specialty chemicals has remained stable.

TABLE 6

CRUDE IODINE: WORLD PRODUCTION, BY COUNTRY[1]

(Metric tons)

Country[2]	1986	1987	1988	1989[p]	1990[e]
Chile	3,076	[r]3,181	3,967	[re]3,845	5,029
China[e]	500	500	500	500	500
Indonesia	6	8	10	14	15
Japan	7,389	7,014	7,451	7,592	7,500
U.S.S.R.[r]	2,000	2,000	2,000	2,000	2,000
United States	W	W	998	1,508	[3]1,973
Total	[4]12,971	[r4]12,703	14,926	15,459	17,017

[e]Estimated. [p]Preliminary. [r]Revised. W Withheld to avoid disclosing company proprietary data.
[1]Table includes data available through May 31, 1991.
[2]In addition to the countries listed, New Zealand also produces elemental iodine, but data are not available and available information is inadequate for formulation of reliable estimates of output levels.
[3]Reported figure.
[4]Excludes U.S. production.

[1]Rosene, M. R. Silver Removal With Halogen Impregnated Non-carbon Adsorbents. U.S. Pat. 4,396,585, Aug. 2, 1983.

[2]Hunt, M. Beat the Drums Faster. Materials Eng., v. 107, No. 7, 1990, pp. 31–35.

[3]U.S. Embassy, Santiago, Chile. Israel's Growing Investment in Chile's Mining Sector. State Dep. Telegram 2612, Mar. 30, 1990, 4 pp.

[4]Mining Journal (London). Yolanda Debate. V. 315, No. 8102, 1990, p. 472.

[5]U.S. Embassy, Santiago, Chile. Chile-Hunt Oil Company Finds Gas in the Salar de Atacama. State Dep. Telegram 3439, May 3, 1990, 2 pp.

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